The Influence of Impurities on the Interactions Responsible for Superconductivity

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The nature of impurity resonances in electron energy bands is discussed for both simple- and transition-metal impurities in both simple- and transition-metal matrices. The effects of such resonances on the phonon-induced electron-electron interaction and on the dynamically screened Coulomb interaction is also discussed. It is concluded that transition-metal impurities in simple metals and vice versa will reduce the transition temperature if resonances occur, but that no corresponding effect occurs for transition-metal impurities in transition metals. It is suggested that if anomalies do arise in the latter case, they are more likely to be attributable to virtual local moments.

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I. INTRODUCTION

There is an extensive body of experimental facts[1] suggesting that certain impurities have influences upon the interactions responsible for superconductivity which cannot be encompassed within a theory based on the assumption of "normal" alloying behavior.[2]

Alloys which behave "normally" are defined as those for which the simple band and phonon pictures remain valid when supplemented by nonresonant impurity scattering, as in the Anderson theory of dirty superconductors.[3] Deviations from normal alloying behavior can thus occur in two obvious ways: 1) Instead of a smooth variation of the band structure with concentration, impurity resonances can occur at low concentrations[4,5] which can merge into impurity bands at higher concentrations.[6] 2) Similarly, impurities can produce resonant local modes in the phonon spectrum of the host material.[7,8] The purpose of the present paper is to discuss the implications of the first of these two deviations from normal alloying behavior for superconductivity.

A more subtle deviation from normal alloying behavior in superconductors arises from the series of impurities Cr through Co. These can cause either a) impurity resonances in the spin-density wave and spin-rotation wave spectrum of the conduction electrons or b) stable local moments. Because the present theoretical understanding of stable local moments[9-12] and of their influence on superconductivity[13] is relatively satisfactory, we have confined our attention to

the impurity resonances a). We have found significant consequences of spin-dependent impurity resonances for superconductivity. Time does not permit the reporting of our treatment of such resonances and their consequences here. We do, however, indicate the circumstances in which the spin-independent resonances cannot be important, whereas the spin-dependent resonances can.

II. RESONANT IMPURITY LEVELS

We are concerned here with impurity-induced changes in superconducting transition temperatures of impurity concentrations of less than $\sim$10%. We suppose that superconductivity arises from interactions between pairs of Landau quasi-particles which consist of a phonon-induced part and a dynamically-screened Coulomb part. Changes in the transition temperature thus arise from changes in the corresponding two parts of the Kernel in the BCS integral equation.

It is convenient to make a simple square-well approximation to the parts of the Kernel in the form introduced by Tolmachev[14] and discussed by Garland[2] and others. The transition temperature T_c is then given by

$$\ln \frac{1.14\Theta}{T_c} = -\frac{1}{K_{eff}} \tag{1a}$$

$$K_{eff} = K_{ph} + K_C^* \tag{1b}$$

$$K_C^* = K_C/(1 + K_C\sigma) \tag{1c}$$

$$\sigma = \ln \xi / k_B \Theta \qquad (1d)$$

for "normal" alloys and pure metals. In Eqs.(1a-d), Θ is the cut-off, expressed as a temperature, of the phonon-induced Kernel, K_{ph}, and may be taken equal to the Debye temperature Θ_D. Similarly, ξ is the cut-off in energy of the Coulomb Kernel K_C.

We confine discussion to simple metals and transition metals, which defines four groups of alloys:[15] 1) simple-simple, 2) simple-transition, 3) transition-simple, and 4) transition-transition. Simple-simple alloys, group 1, are normal in behavior and will not be considered further.

As regards group 2, a transition-metal impurity can be expected to introduce five localized d-states within or below the conduction band of a simple metal, provided the difference in atomic potential is sufficiently great. The states will be grouped into one 3-fold and one 2-fold degenerate level about a c. of g. $\bar{E}_d$, with a crystal-field splitting $\hbar\omega$. Such a resonant level will remain narrow even within the conduction band because of the small percentage of d-character of the conduction band states nearby in energy. The localized d-states may be regarded as derived from the nearest Bloch states of the matrix which have the corresponding symmetry. In an A-subgroup matrix the appropriate Bloch states are thus moved down towards the Fermi level to form localized states. In B-subgroup matrices the reverse is true, the impurity levels having been split off

the top of the occupied d-band.

If the impurity levels lie both above or both below the Fermi level, they have no significant effect on K_{eff} and hence, from Eq.(1) on T_c. This follows both from the principle of spectroscopic stability[16] and the smallness of matrix elements between the impurity states and the conduction-band states. On the other hand, if the impurity levels straddle the Fermi level, the principle of spectroscopic stability does not apply, and also the pertinent matrix elements, those connecting the two levels of the same impurity, are significantly larger. One could thus expect a significant influence of impurities on superconductivity if the crystal-field splitting is less than, say, 0.5 eV. In as much as crystal- or ligand- field splittings in ionic environments are of order 1 eV,[17] it is reasonable to suppose the crystal-field splitting to be reduced to nearly an order of magnitude less by screening effects and the absence of covalency effects in a simple metal.

The impurity levels change T_c through their effect on the magnitudes of K_{ph} and K_C in Eq.(1); their influence through the cut-offs ξ and $\bullet$ is negligible. Both K_{ph} and K_C are affected by the resonant levels primarily through their contribution to the dynamic dielectric function, which screens the electron-ion-core interaction in K_{ph} and the Coulomb interaction in K_C. The change in K_{ph} is, very roughly, for a concentration C_d of impurities,

$$\Delta K_{ph} = C_d \frac{2C\hbar\omega}{(k_B\Theta)^2 - (\hbar\omega)^2} K_{ph}, \qquad (2)$$

where we have absorbed the uninteresting factors into the constant C and X is the impurity concentration. When h $k_B\Theta$, as is likely, ΔK_{ph} is thus repulsive. The change in K_C is, also very roughly,

$$\Delta K_C = C_d \frac{C'\hbar\omega}{(\Delta E)^2 - (\hbar\omega)^2} K_C. \qquad (3)$$

In Eq.(3) the constant C' is nearly the same as C in (2), and ΔE is an appropriate difference of normal-state quasiparticle energies. As could have been expected, the change of the Coulomb interaction is attractive and of the Bardeen-Pines type[18] because it arises from the virtual exitation of the impurity atom by one electron and subsequent deexcitation by a second electron in exact analogy with the virtual exchange of phonons. For typical simple-metal superconductors K_{ph} is of order three times greater than K_C^* in magnitude. Analysis of the influence of a square-well representation of ΔK_C on T_c suggests therefore that ΔK_{ph} is nearly an order of magnitude more important than ΔK_C. Rough numerical estimates of C suggest in turn that a 5% addition of impurity could reduce T_c by nearly a factor of 2, i.e., $\Delta T_c/T_c \sim -0.3$ to -0.7 for $C_d \simeq 0.05$ and $\hbar\omega \simeq 0.2$ eV. However, effects of this sort should be greatly reduced in importance when impurity band formation sets in to the point where band widths

become comparable to the crystal-field splitting. From what one knows of d-band widths in transition metals, one would guess this to occur at concentrations somewhat below 10%.[19]

Turning now to group 3, simple metal impurities will have a tendency to split off resonant localized d-states from the d-band of a transition metal again provided the difference in atomic potential is sufficiently great. These will be above the d-band for A-subgroup impurities and below the d-band for B-subgroup impurities. Because the density of states within the d-band is relatively high and because these levels are in general well away from the Fermi level, they have no important direct influence on the dielectric function and hence T_c. The influence they do have is subtle though simple, and requires a fairly detailed theory of impurity level formation for its understanding.

We have developed such a theory by generalizing the treatments by Koster and Slater[4] and by Clogston[5] of the localized impurity potential to arbitrary band structure. There results for the perturbed density of states

$$N(E) = N_o(E) - \frac{1}{\pi} \sum_{\gamma} \operatorname{Im} \left\{ \frac{\langle o\gamma | \frac{dR_o}{dE} | o\gamma \rangle V_{o\gamma}}{1 - \langle o\gamma | R_o | o\gamma \rangle V_{o\gamma}} \right\} \qquad (4)$$

where $N_o(E)$ is the unperturbed density of states, V is the impurity potential, and R_o is the unperturbed resolvent

$$R_o = [E - i\alpha - H_o], \quad \alpha \to 0^+ \quad . \qquad (5)$$

Matrix elements are taken in the crystal coordinate representation,[20] $|\ell\gamma\rangle$ referring to the Wannier function of symmetry type plus ordinal index γ centered about the ℓ^{th} unit cell.

We have assumed that $\langle \ell\gamma | V | \ell\gamma \rangle = V_o \, \delta_{o\ell} \, \delta_{o\ell'} \, \delta_{\gamma\gamma'}$ A study of Eq.(4) reveals that changes in the density of states are closely related to those features of $N_o(E)$ which arise from the critical point structure of the energy bands. We have constructed a simple model of a d-subband with a minimal set of critical points[21] superposed upon a nearly-free-electron band and have used this model as a basis for detailed numerical calculations of $N(E) - N_o(E)$ for various cases.

We find that a simple-metal impurity can give rise to very narrow impurity resonances within the nearly-free-electron band and outside the d-band for sufficiently large $V_{o\gamma}$ ($\gtrsim$ 1/3 the subband width). These narrow resonances are accompanied by antiresonances in the vicinity of maxima in the d-bands which extend over about half a subband. Thus, when the density of states at the Fermi level is relatively large, it can be reduced significantly by the antiresonances. This reduction of the density of states manifests itself in turn by a reduction of K_{eff} and hence of T_c. Very rough numerical estimates suggest that reductions of the transition temperature are relatively small for 5% of simple metal added to a transition metal, i.e., $\Delta T_c/T_c \sim -0.05$ to -0.1. It is thus not clear that we have elucidated all of the operant factors for transition-simple alloys.

The above theory of impurity levels contained in Eq.(4) is useful also for our discussion of group 4, transition-metal impurities in transition-metal matrices. It is commonly supposed that very sharp impurity resonances can occur in such situations, as appears to be demanded by a variety of experimental results. Explicit numerical calculations based on the model mentioned above show that impurity resonances indeed occur close to, but outside of, peaks in the density of states (i.e., they are associated with saddle points in the energy surfaces), but that their widths are of the same order as the subband widths. If experimental results appear to indicate the existence of narrow resonances near the Fermi energy, it seems unlikely to us that the indicated resonances occur in the band structure. It seems much more likely that they occur in the spin-density wave and spin-rotation wave spectra, where we have been able to show that narrow, or sharp, low-energy resonances are possible which are essentially equivalent to virtual local moments.

Although the level structure of a transition-transition metal alloy can thus be more complex than would be indicated by a band picture, the kind of spin-independent level structure which would probably arise would probably also lead to variations in T_c indistinguishable from those expected from normal alloying behavior. Any observed deviations from new interactions involving virtual excitations of the spin-independent resonances, particularly if the elements Cr-Co

are the impurities in matrices in which they do not form local moments. Exchange plays an important role in these interactions so that in this sense they resemble interactions proposed earlier by Matthias.[22]

The conclusions reached in this paper appear qualitatively consistent with the published experimental data, as presented and discussed, for example, by Matthias, Geballe, and Compton in ref. 1. It is, however, impossible to draw quantitative conclusions about individual alloy systems from our theory in the absence of detailed experimental information on the impurity states themselves.

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The noble metals thus do not fall into the category of simple metals. Despite the fact that the d-shells are sull, the d-electrons in noble metals cannot be considered as core electrons. The d-band is about 3 volts wide, and hybridization with the conduction band accounts for half the cohesive energy. For a discussion of impurity levels associated with transition metal impurities, the noble metals must either be lumped together with the transition metals or classified separately as a third group.

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here, Hund's rule comes into play so that the one-electron levels will be occupied so as to give a net spin i.e., stable local moment. The mechanism for the reduction of T_c by paramagnetic impurities discussed in ref. 14 then comes into play. Our results, however, imply that changes in ϵ associated with the impurity level structure are of comparable importance to the exchange scattering of ref. 14 even when permanent moments are formed.

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